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Published in:
Scripta Materialia

DOI:
10.1016/S1359-6462(01)01007-7

Publication date:
2001

PERGAMON

Scripta Materialia 45 (2001) 169–175

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Antimony segregation at copper/manganese-oxide interfaces studied with analytical transmission electron microscopy

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Received 3 January 2001; accepted 6 March 2001

Keywords: Segregation; X-ray energy dispersive analysis; Transmission electron microscope; Composites; Interface

Introduction

Metal/ceramic interfaces play an important role in advanced materials. Important examples are dispersion hardened alloys [1], ceramic coatings and microelectronic packaging [2]. Impurity segregation to these interfaces may have a large influence on the atomic scale properties and in several cases on the macroscopic properties. In contrast to segregation at grain boundaries in metals and in ceramics, segregation at metal/ceramic hetero-interfaces received only scant attention. Of the few studies of segregation at metal/ceramic interfaces, we mention here 1D-atom probe field ion microscopy (APFIM) measurements of Ag segregation at {1 1 1} Cu/MgO interfaces and of Au segregation at {1 1 1} Ag/CdO interfaces [3,4] and analytical scanning-transmission electron microscopy (STEM) results obtained for segregation at the Al{1 1 1}/α-Al_2O_3 (0 0 0 1) interface [5]. Until recently, we could demonstrate only indirectly the presence of segregation of solute atoms at metal/ceramic interfaces [6]. This was only recently supported by subnanometer 3D-atom probe investigation of segregation at MgO/Cu ceramic/metal heterophase interfaces [3,4]. For X-ray energy dispersive spectrometry (EDS) measurements, a TEM with a field emission gun provides a very coherent and high intensity electron beam. The high brightness together with a high accelerating voltage and a thin specimen make it possible to use a small probe size and perform chemical analysis on areas of nanometer size. In contrast to the Ag(Sb)/Mn_3O_4 and

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PII: S1359-6462(01)01007-7

Cu(Sb)/MgO systems, the Cu(Sb)/MnO system is well-suited for investigation by EDS due to the flat (without steps or ledges) and large facets of the MnO precipitates. For instance, MgO precipitates in Cu are both much smaller and show more ledges than the MnO precipitates in Cu [7,8].

Experimental procedure

MnO precipitates in pure copper were obtained by internal oxidation of Cu–1.0 at.%Mn. 200 μm thick foil was oxidised at 900°C for 20 h using the so-called Rhines Pack method [9]. After internal oxidation octahedral MnO precipitates were formed in the Cu with a cube-on-cube orientation relation. The precipitates are bounded by atomically flat semi-coherent, oxygen terminated $\{1\,1\,1\}$ interfaces and by very small $\{1\,0\,0\}$ facets (i.e., the precipitate shape is a truncated octahedron). The typical size of the precipitates is 300 nm. Detailed information about MnO precipitates in Cu is present in Refs. [8,10].

Antimony was introduced by annealing the specimen, together with Sb separately present, in an evacuated quartz tube at 700°C for 168 h. During this treatment the antimony evaporates and can diffuse into the Cu containing the MnO precipitates. After such a vapour treatment the concentration of Sb will be somewhat higher for parts of the Cu foil closer to the original location of the Sb as was measured by EDS in an SEM. However, the same technique revealed that a more or less homogeneous Sb distribution throughout the cross-section is achieved during the annealing treatment.

TEM samples were prepared by dimpling and ion milling using a Gatan PIPS. Just before putting the samples in the TEM for chemical analysis, each sample was ion milled at 4 kV for about 3 min, to remove contaminant surface layers. The analytical TEM measurements were performed in a JEOL 2010F. A double tilt beryllium holder with a range of $\pm 30°$ for both tilt directions was used to hold the samples. To obtain an EDS spectrum at the $\{1\,1\,1\}$ Cu/MnO interface, the Cu matrix is aligned in its $\langle 1\,1\,0\rangle$ zone axis. In this way the planar interface is observed edge-on which avoids mixing of the signals from the metal matrix and the oxide precipitate. It was not always possible to find a precipitate with a position that, when it was tilted to the $\langle 1\,1\,0\rangle$ direction, could meet all the optimum orientation conditions. However, during EDS measurements the specimen was never tilted away from the detector and the tilt towards the detector did not exceed 10°, in order to minimise the influence of absorption and spurious X-rays, respectively. The dead time was usually around 10% with a time constant of 50 μs for the processor to evaluate the signal.

The EDS spectra of the Cu/MnO interfaces were obtained in 25–40 s. The high brightness of the field emission gun allows for a combination of this short time of measurement, a small probe size and a thin specimen. The small thickness of the specimen allows us to ignore the effects of absorption and fluorescence and perform only a correction for the atomic number Z (thin film approximation). The number of photons collected from the elements under investigation were converted to relative concentrations with the Cliff–Lorimer ratio technique [11] in the thin film approximation.

The differences in energy of the Cu, Mn and Sb peaks were large enough to have no ambiguity about the source of these peaks. This is an advantage over electron energy loss (EELS) measurements, where the Sb and O peaks strongly overlap. Only the overlap of the O-K and Mn-L peak could give rise to relatively large variations in their apparent concentration. A cold finger, cooled to liquid nitrogen temperatures, was used to reduce the hydrocarbon contamination.

The spectra were obtained using the smallest possible probe size, which is, at optimum conditions, 0.9 nm at FWTM (0.5 nm FWHM). Composition profiles were obtained by moving the electron beam perpendicular to the interface and recording a number of spectra. The positioning of the electron beam at the start of a line scan was performed by looking at a bright field image of a precipitate. A computer could control the direction and length of the steps of the line-scan.

Results and discussion

A composition profile obtained across a planar interface, with the direction of the electron beam parallel to the interface, is depicted in Fig. 1. The absolute and relative Sb concentration (defined as $100 \times C_{Sb}/(C_{Sb} + C_{Cu})$) with concentrations in at.% are plotted versus the secondary y-axis and the error bars represent $\pm 2\sigma$ based on Gaussian statistics. The line scan depicted in Fig. 1 has a relatively smooth profile in which the interface can be discerned relatively easy. This is not the case for all concentration profiles. The drift of the beam will influence not only the values for the concentration (due to an enlargement of the effective probe size) but also change the relative position at the interface and thereby change the shape of the interface. In practice, the length of

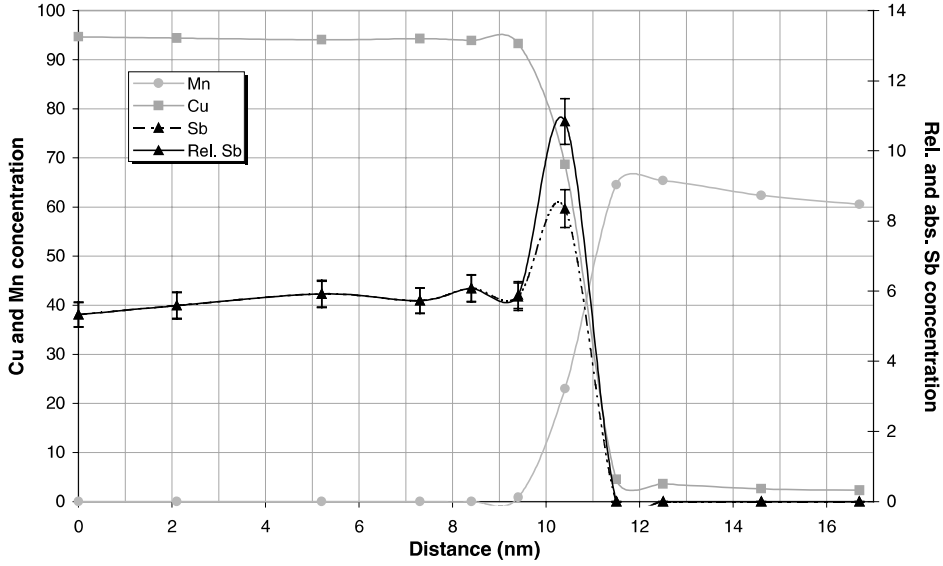

Fig. 1. Composition profile across a {1 1 1} Cu/MnO interface obtained by EDS.

the interface profile will always either be expanded or reduced (or even missed) because of the drift. Because of the drift it was important to keep the duration of a measurement as short as possible. The minimum counting time appeared to be about 35 s. A shorter counting time made it difficult to detect the low Sb concentrations and resulted also in a large spread in the values for the concentration in homogeneous areas.

Spectra that were measured on MnO precipitates showed a small Cu signal. Spurious X-rays are the most plausible explanation for this Cu signal. Another explanation could be that Cu is dissolved in the MnO precipitate, but that is not expected. STEM [12] and EELS [3,4] measurements have revealed a nearly complete separation of MgO from Cu and it is most likely that the same is true for the Cu/MnO system. Most ceramics have a negligible solute solubility for metals such as antimony. This was confirmed by our EDS measurements on the MnO precipitate, where no antimony signal was measured. Therefore, when it is assumed that Sb is only dissolved in the copper, the relative Sb concentration ($C_{rel.}$ Sb) defined above is a proper measure for the detection of segregation.

Spectra from the Cu/MnO interface were also obtained by separate measurements, where the electron beam was positioned at the interface by looking at a bright field image of the precipitate. The data from the composition profiles together with the data from the separate measurements are used for the determination of the segregation to the interface. To incorporate all the measurements the interface is determined on basis of the amount of copper or manganese, disregarding the relative position. When the concentrations of Cu and Mn have values in between the values in the bulk and in a MnO precipitate it can be assumed that the measurements were taken on the interface. With this method the influence of the beam drift on the relative position is decreased. Fig. 2 shows a composition profile that is plotted against the amount of copper instead of the relative position. The interface is defined as the positions where the Cu or Mn concentration is between 10% and 90% of their maximum value. Fig. 2 shows that the absolute Sb concentration is higher at the 'end' of the interface where the Cu concentration is almost 90%. The relative Sb concentration is clearly higher than in the bulk, along the full length of the interface.

All seven interfaces we analysed showed a clear enhancement of Sb at the interface. For an ideal line scan perpendicular to the interface only at one location of the electron probe an Sb enrichment is observed (cf. Fig. 1). In almost every measurement the enrichment of Sb is detected in conjunction with Mn, which means that the enrichment does not continue very far into the copper matrix and thus corresponds to Gibbsian segregation. Table 1 shows the results from the seven interfaces. The third column displays the average relative Sb concentration in which all the interfacial measurements (in between 90% and 10% of the Cu-signal of the matrix) in which a significant Sb intensity could be detected, are incorporated. In some cases we could not detect any Sb at a position which was, on the basis of the copper and manganese concentration, at the interface. This occurred when the copper concentration had already dropped to slightly above 10%. Although in this case the relative Sb concentration can be higher than in the matrix, the absolute Sb concentration will have become near to 1 at.% which hampers the detection of Sb. So, these apparent zero values for the Sb concentration were not

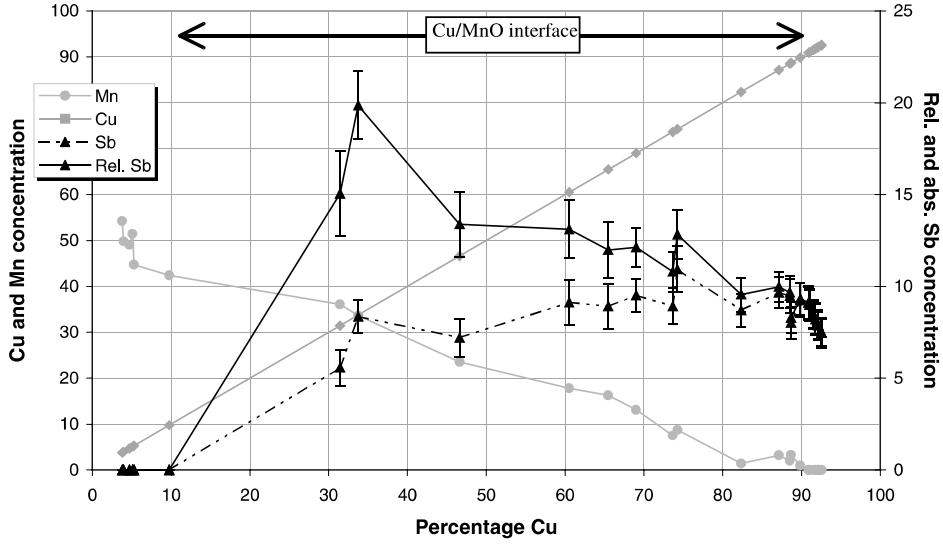

Fig. 2. A composition profile, where the position relative to the interface is derived from the copper concentration.

Table 1
Relative Sb enrichment at seven Cu/MnO interfaces[a]

Interface	Sb concentration in Cu matrix (# measurements)	Average rel. Sb concentration at interface (# measurements)	Maximum rel. Sb concentration at interface	Average enrichment (%)	Maximum enrichment (%)
1	6.2 ± 0.3 (5)	7.4 ± 0.6 (2)	7.5 ± 0.8	19 ± 11	21 ± 14
2	5.9 ± 0.2 (7)	9.7 ± 0.4 (9)	14.8 ± 2	64 ± 9	151 ± 35
3	7.9 ± 0.2 (12)	18.7 ± 0.5 (6)	30.6 ± 1.5	137 ± 9	287 ± 21
4	6.9 ± 0.2 (15)	16.5 ± 0.6 (13)	21.6 ± 2.6	139 ± 11	213 ± 39
5	5.8 ± 0.4 (6)	10.8 ± 0.7 (1)	10.8 ± 0.7	86 ± 18	86 ± 18
6	6.3 ± 0.2 (4)	10.8 ± 0.2 (23)	16.0 ± 1.8	71 ± 6	154 ± 30
7	8.1 ± 0.3 (8)	12.0 ± 0.4 (13)	19.9 ± 1.9	48 ± 7	146 ± 25
Average	6.7	12.3	17.3	81	151

[a] The relative Sb concentration is defined as $100 \times C_{Sb}/(C_{Sb} + C_{Cu})$.

used in the calculation of the average Sb concentration. The fourth column shows the maximum value of the relative Sb concentration measured at the interfaces. The counting time per measurement was 35 s for all interfaces except interface 4 and 5 where the counting times where respectively 25 and 40 s. In columns 5 and 6 the enrichment at the interface based on the relative Sb concentration measured (on several locations) in the Cu matrix near the interface is given. It is clear from the values in Table 1 that there is a significant segregation at all the interfaces if one considers either the average or the maximum Sb concentration.

Under the assumption that all excess Sb atoms are located on a single monolayer at the Cu/MnO interface, an estimate for the relation between the number of excess atoms

and the measurable average relative Sb concentration can be obtained. Assuming one effective Sb monolayer directly at the interface, an electron probe of 2.5 nm (which holds for a copper specimen of 50 nm thickness and a 200 kV electron beam with a size of 0.9 nm at the entrance of the specimen [13]) perfectly aligned on the interface and taking the distance between the Cu layers and the Sb layers perpendicular to the interface 0.2 nm and assuming 6.7 at.% Sb in the Cu layers, the estimate for the measurable Sb concentration is 25%. The value for the average relative Sb concentration we obtained is considerably less, which indicates that the effective Sb coverage in our system is less than one monolayer. Under the same assumptions the average relative Sb concentration of 12.3 at.% we determined experimentally for the seven interfaces would correspond to an effective Sb coverage of approximately 1/3.

From Table 1 it can be seen that the maximum Sb concentration at the interface is on average more than two times as large as the concentration in the bulk. The two lowest values in the last column (interface 1 and 5) are from measurements where two and one measurement(s) were taken at the interface, respectively. This seems to indicate that the reason for the relatively low concentration at these interfaces has nothing to do with the enrichment itself but is due to the small number of measurements, where probably the optimum point for measuring the maximum Sb enrichment is missed. The relative Sb concentration varied across the interface and the relative Sb concentration is generally highest when most of the signal originates from the MnO precipitate, as should be expected. It is possible that none of the measurements at interface 1 and 5 were obtained from a position where the Sb concentration is at a maximum value. Disregarding these two values gives an average maximum enrichment of $190 \pm 14\%$.

Although it appeared reasonable to consider the Sb concentration relative to the copper concentration, the result that Sb segregates to the Cu/MnO interface does not crucially depend on this choice. When the absolute Sb concentration is considered (i.e., not relative to the copper concentration) a significant enrichment can still be detected. Obviously, the absolute segregation level is lower and can only be detected at the start of the interface where the Mn and O concentration are still relatively low.

Conclusions

Cu/MnO interfaces were obtained by internal oxidation of Cu–1 at.%Mn. Subsequently antimony was introduced in the system by annealing it in an evacuated quartz tube containing a limited amount of Sb vapour. In the Cu matrix the Sb concentration turned out to be about 6 at.%. No Sb could be detected within MnO precipitates, which indicates that the solute solubility Sb in MnO is negligibly small. For this reason it is justified to determine the amount of Sb relative to the sum of the Sb and Cu concentration.

A total of 124 spectra, near or at seven parallel {1 1 1} interfaces, were obtained by EDS. For every investigated interface the relative Sb concentration is found to be significantly higher across the interface than all the concentrations measured in the copper matrix at distances further away from the interface. The maximum relative Sb

concentration at the interface was about 2–3 times the average Sb concentration in the copper matrix. The average relative Sb concentration gives an estimate of the Sb coverage at the interface of 0.3–0.4 effective monolayers (i.e., assuming all excess Sb in one monolayer at the interface). Considering the absolute Sb concentration (i.e., not relative to the copper concentration) the enrichment of Sb at the interface is still significant although obviously it is considerably smaller than the enrichment of the relative Sb concentration.

The results show that X-ray EDS, performed in a TEM with a field emission gun and a 0.9 nm probe size, provides an adequate method to demonstrate, in a direct and unambiguous way, the segregation of Sb at the Cu/MnO interface.

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